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Effects of the addition of ulexite to the sintering behavior of a ceramic body

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The aim of this study was to investigate the effects of the addition of ulexite to the sintering behavior of a ceramic body. Ulexite is a boron mineral that is known as sodium calcium borate. The effects of ulexite, as a powerful flux, on the properties such as the water absorption, bending strength, and shrinkage and on the colors of ceramic tiles were studied. The microstructures of a standard and tiles with the additive were analyzed using a scanning electron microscope (SEM). The properties of with ulexite added tiles were compared with that of standard tiles and it was concluded that tiles having the additive had more favorable physical properties than the standard ones. Adding ulexite decreased the sintering temperature of the tiles, which in turn led to an increase in the bending strength of the tiles, a decrease in water absorption, and an increase in shrinkage. The SEM analyses have shown that ulexite additions increased the vitrification in the body.

Key words: Ulexite, Ceramic, Sintering, Microstructure, Boron mineral.

Introduction

Ulexite is a boron mineral which includes % 43 B_2O_3 (boron oxide). Pure boron element does not exist in nature; rather it is found generally as boron oxides. Boron minerals, produced as the compounds of boron oxide and alkaline or earth alkaline elements exist widely in nature. Although there are many varieties of boron minerals in nature only a small amount of these varieties can be used commercially. Some of commercially available boron minerals are colemanite, tincal and ulexite. Colemanite which is a calcium borate mineral has a monoclinic crystal structure and its chemical composition is $Ca_2B_6O_{11}.5H_2O$. Tincal (crude borax) is a sodium borate mineral, it has a monoclinic crystal structure and its chemical composition is $Na_2B_4O_7.10H_2O$. Ulexite is a sodium calcium borate mineral. Its chemical composition is $NaCaB_5O_9.8H_2O$. The water in the structure of ulexite exists as 3 moles of hydroxyl groups and 5 moles of crystal water ($NaCa[B_5O_8(OH)_6].5H_2O$). Ulexite exists as a white parallel fiber has a triclinic crystal structure and it has relatively low water solubility, % 0.5 at 25 °C [1, 2].

In Turkey commercially produced boron minerals are colemanite, ulexite, and tincal. These borate mineral are produced in large amounts in Turkey where ulexite is produced in Balikesir-Bigadic. In Bigadic, an ulexite ore is produced in open mines. A ulexite process is carried out in the ore preparation facilities near ore mines in Bigadic. Ulexite is enriched via processes like crushing, wetting in water, washing in a tumbling mill, sieving, triage and classification, produced in different grain sizes and chemical compositions as concentrated ulexite, and offered for sale. A major portion of the concentrate ulexite produced is exported.

Boron minerals are used extensively in the glass and ceramic industry as vitrification and flux agents. For this reason, boron and boron compounds are added to glaze compounds. Boron (B), boric oxide (B_2O_3), tincal (borax), colemanite, and ulexite have different melting temperatures. It should be noted that they all have different melting points. Sener *et al.* [3] reported that the melting point of the ulexite mineral is 850 °C, whereas boric oxide (crystal B_2O_3) has a melting temperature of 2180 °C.

Many researchers have investigated the use of boron mineral and waste as additives in ceramic tiles. When boron mineral and waste were mixed with the tile slurries improvements were observed in the physical properties of the tile. Olgun *et al.* [4] reported that adding tincal waste and bottom ash to a wall tile slurry increased the fired strength of the tiles. The strength of tiles including tincal waste is greater than that of standard tiles and that of tiles including bottom ash. With an increase in the amount of tincal waste addition water absorption of tiles were observed to decrease. Kurama *et al*. [5] found that borax waste increased the vitrification and thereby provided better technological features. Bayca *et al*. [6] observed that tincal can be used as a flux material in ceramic bodies due to its favorable effects on the water absorption and fired strength.

Colemanite, kaolin, and a K-feldspar mixture to be calcined were added to floor tile slurry. Increasing the amount of additive generally caused higher shrinkages and lowered water absorption. Moreover, strength values were improved. The low sintering and melting point of the additive compared to the other components of the floor tile recipe positively affected the technical properties

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of the samples [7]. It was found that the fired strength of the bodies containing the tincal waste was increased compared to the standard bodies [8]. When borax waste was added to the floor tile body, it increased the strength of the body and decreased the water absorption and porosity [9]. When borax waste was used in the frit composition in floor tile glazes instead of dolomite, albite, and boric acid better glaze features were obtained [10].

The aim of this study is to investigate the effects of the incorporation ulexite on the sintering behavior of a ceramic body. For this purpose, a series of tests were carried out. Because the firing conditions of the samples in a laboratory furnace are different from industrial furnace conditions, an industrial furnace was chosen for the firing process in these experiments.

Materials and Methods

Materials

The ulexite used in the experiments in this study was obtained from Eti Mine Bigadic Boron Works (Balikesir, Turkey). The Bigadic mine is worked by an open pit operation. Ulexite ores from open pit mines are treated in the Bigadic concentrator. Ulexite is produced in large tonnages in Turkey. The chemical compositions of the standard body and ulexite mineral are given in Table 1.

X-ray diffraction analysis (XRD Phillips X'Pert Pro) of ulexite is given in Fig. 1. The main mineral is ulexite. The other minerals are smectite, calcite, quartz and strontianite in lesser proportions.

Methods

Ulexite was dried to a constant weight at room temperature for 7 days. Dried ulexite was crushed by a jaw crusher. Using clay, albite, pegmatite, quartz, and ceramic waste in the amounts shown in Table 2, standard floor tile bodies were prepared. To these tiles ulexite was added in between 0-6% proportions.

Ulexite, clay, pegmatite, quartz and ceramic waste were milled by a wet method in a ceramic ball mill and this compound was sieved to pass through a 63-μm screen to obtain suitable powders for pressing. Five different batches were prepared by mixing different amounts of the standard body and ulexite (see Table 2). The materials were mixed in a ball mill using an alumina-milling media for 20 minutes. The mixtures were compressed by unaxial pressing at 60 MPa. As a result, the tiles obtained were 100 × 50 × 10 mm. Firing of tiles was carried out in a commercial liquid petroleum gas roller furnace at 1192 °C for a soaking period of 35 minutes. The sintered ceramic tiles were tested for their fired bending strength, linear shrinkage and water absorption. The microstructure of sintered tiles was analyzed with a JEOL JSM 6060 scanning electron microscope (SEM).

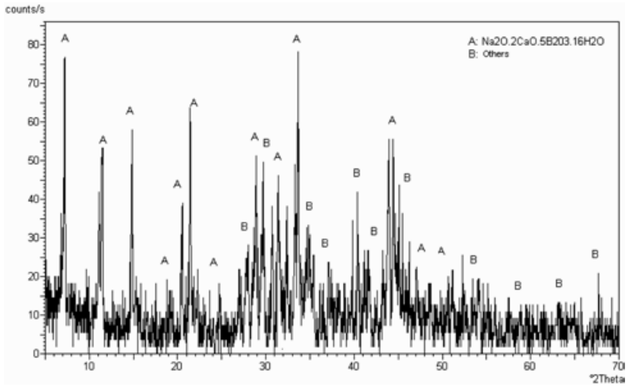

Fig. 1. X-ray diffractogram of ulexite.

Table 1. Chemical analysis of standard floor tile body and ulexite

Oxides	Standard body, wt%	Ulexite, wt%
SiO_2	63.66	3.04
Al_2O_3	17.51	0.05
Fe_2O_3	1.87	0.24
TiO_2	0.67	-
CaO	0.54	17.13
MgO	1.65	1.39
Na_2O	2.70	4.67
K_2O	2.02	-
B_2O_3	-	38.01
SrO	-	0.80
Others	-	0.64
LOI	9.38	34.03

Table 2. Ceramic body formulations (%)

Materials	S wt%	T1 wt%	T2 wt%	T3 wt%	T4 wt%	T5 wt%
Clay	52	52	52	52	52	52
Albite	32	32	32	32	32	32
Pegmatite	6	6	6	6	6	6
Quartz	6	6	6	6	6	6
Ceramic waste	4	4	4	4	4	4
Ulexite	0	0.5	1	2	4	6

Linear Shrinkage

The linear shrinkage of samples was determined after drying and firing. The total shrinkage, which is the linear shrinkage from the wet state to the fired state, was also determined. The shrinkage was calculated as follows:

$$S = \frac{Li - Lf}{Li} \cdot 100 \tag{1}$$

where S is the shrinkage percent. L_i initial length of the body (mm), L_f is the final length of the body (mm).

Linear shrinkage tests of the unglazed fired tiles were carried out using the previously mentioned method in this investigation.

Water absorption

The sintered tiles were dried to a constant weight, cooled to room temperature, and then weighted. The tiles were immersed in distilled water and boiled for three hours. The heating was stopped and the tiles were allowed to remain immersed in the water for 24 h. The tiles taken out and excess water was removed from their surfaces by wiping with a damp cloth. The tiles were again weighted. The water absorption was calculated using the formula:

$$WA = \frac{wf - wi}{wi} \cdot 100 \quad (2)$$

where WA is the water absorption (%), wi is the dry mass (g), wf is the fired mass (g).

In the experiments, water absorption tests of the unglazed fired tiles were carried out using the previously mentioned method.

Bending strength

The sintered tiles were measured to determine the sample width and the sample thickness. Measured tiles were put onto a strength machine. The distance between supports was measured and then the tiles were crushed using the strength machine. The breaking load of the tile was read from the machine. The bending strength was calculated using the following formula:

$$BS = \frac{3FL}{2bh^2} \quad (3)$$

where BS is the bending strength (MPa), F is the breaking load (N), L is the distance between supports (mm), b is the sample width (mm), and h is the sample thickness (mm).

In this study, the fired bending strength tests of 100 × 50 × 10 mm unglazed fired tiles were carried out using the previously mentioned method.

Color of the tiles

The colors of the tiles were designated with letters *a*, *b*, and *L*. Positive *a* means the tiles are red, negative *a* means the tiles are green. When *b* is positive color the tiles is yellow, when it is negative the tiles are blue. When the value of *L* equals 100 the tiles are white, when *L* is zero the tiles are black.

Results and Discussion

Fig. 2 displays the water absorption values for standard and ulexite added bodies. The water absorption level of the standard body was 7%. The water absorption level decreased with an increase in the ulexite percentage. A maximum decrease was observed with at 0.5% ulexite addition. The decrease in water absorption level can be caused by the fact that the fluxing features of ulexite the leads to the creation of large amounts of liquid phases. Ulexite plays a strong flux role in the tile body and causes an increase in the vitrification in the body. The vitrified phase gives rise to the filling of open pores which in turn decreases the open porosity. As a result of this, water absorption, which is an indication of body porosity, decreased.

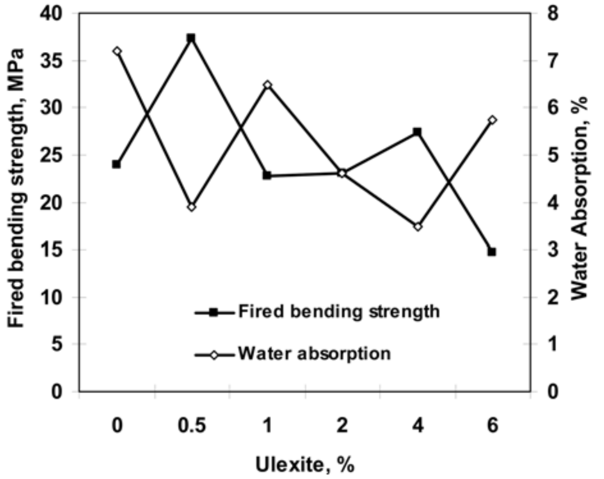

Fig. 2. Water absorption and fired bending strength as a function of ulexite content.

However, the water absorption value increased sharply with 1% and 4% ulexite additions. This can be attributed to the fact that ulexite causes air bubbles which in turn caused the open porosity to increase. Similar results were obtained in previous studies [4, 5, 8].

The water absorption level of standard tiles should not be high. Since the addition of ulexite decreases the amount of water absorption in the tiles, ulexite addition to tiles is recommended.

Fig. 2 also shows the bending (fired) strength values for standard and ulexite added bodies. The standard body has a strength value of 24 MPa. There was a sharp increase in the bending strength value with a % 0.5 ulexite content. The strong fluxing effect of ulexite has increased the vitrification and this in turn has increased the density of the body. The molten ulexite particles in the ceramic body coalesced with others and filled the pores in the body. Thus, increasing the density caused the bending strength to increase. As a result ulexite plays a role as a sintering agent.

However, a decrease in the bending strength value has been observed at % 1 and % 6 ulexite contents. Ulexite caused the creation of bubbles in the body which increased the porosity, however, the density still decreased. A well-sintered and compact body structure was obtained at 0.5% ulexite content. However, increasing the ulexite content increased the glass phase content. This high glass phase content resulted in low strength in the bodies. Bayca et al. [6] reported that tincal caused an increase in the content of glassy phase in the body, which leads to a decrease in the open porosity of the ceramic body. Due to its low melting point, tincal can be used as a flux material in the production of tiles. Luz and Ribeiro [11] concluded that glass powder waste shows an efficient fluxing agent behavior when it is used as an additive in a ceramic mixture. During firing, glass powder waste accelerates the densification process, causing a lower open porosity which yields positive effects on water absorption.

The addition of borates to fuel ash improved the physical and mechanical properties of sintered fuel ash and

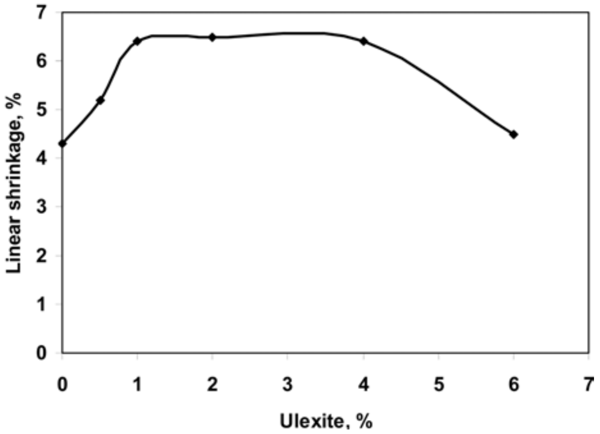

Fig. 3. Linear shrinkage as a function of ulexite content.

significantly reduced the firing temperature [12]. The same effects were observed when ulexite was added to the tile bodies.

Linear shrinkage (dry and fired shrinkage) values for the standard and ulexite added bodies are shown in Fig. 3. The linear shrinkage value of the standard tile is 4%. Ulexite additions increased the shrinkage up to 1% content. Being a strong fluxing material, an ulexite addition has increased the vitrification and hence decreased the porosity in the body. As a result of this, shrinkage has increased. There was not a significant change in the shrinkage of the body between 1-4% ulexite additions. Shrinkage was decreased with a 6% ulexite addition.

Table 3. Color parameters of samples

	S	T1	T2	T3	T4	T5
L	67.88	65.39	66.64	66.3	59.32	59.24
a	+6.23	+6.57	+5.96	+4.36	+3.8	+3.4
b	+22.99	+23.84	+23.38	+20.98	+18.81	+18.89

L, *a*, *b* values for the standard and ulexite added tiles are given in Table 3. The fired color of the standard tile is light red. *L, a, b* values of the tile T1 were not different from the standard values. However, *L, a, b* values of the tiles T4 and T5 were observed to decrease. This decrease has caused the colors of the tiles to darken.

Fig. 4 shows SEM micrographs of the bodies. The lowest open porosity was observed in the T1 tile. This tile has a

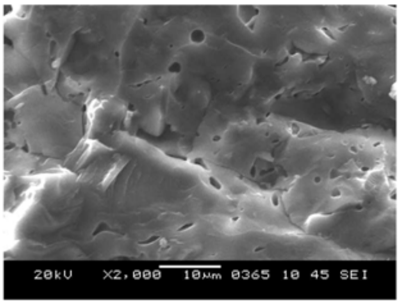

Fig. 4a SEM 0.5% ulexite

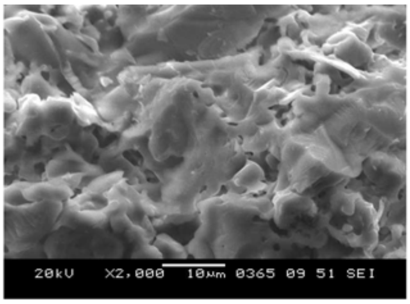

Fig. 4b. SEM 1% ulexite

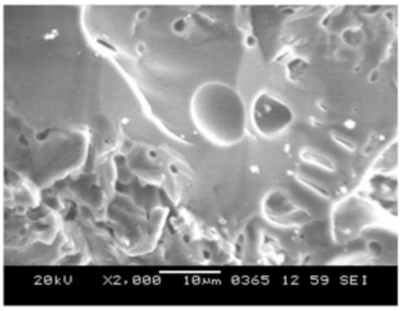

Fig. 4c SEM 2% ulexite

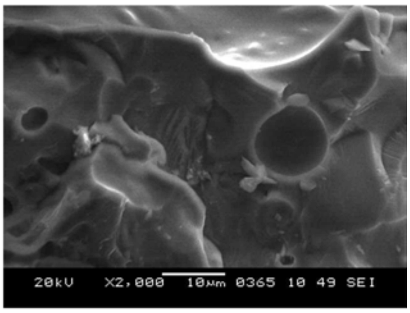

Fig. 4d SEM 4% ulexite

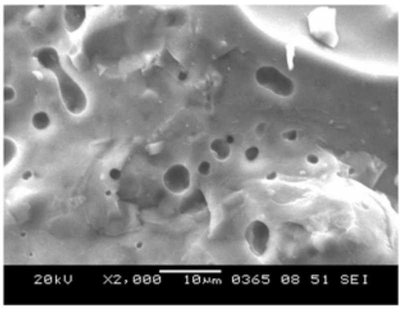

Fig. 4e SEM 6% ulexite

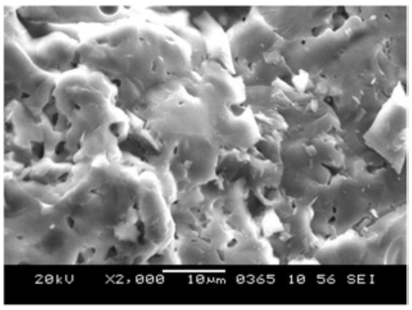

Fig. 4f SEM Standard body

Fig. 4. SEM micrographs of bodies (a) T1, (b) T2, (c) T3, (d) T4 (e) T5 and (f) Standard.

high density because of vitrification and is well sintered. Grain boundaries are seen in tile T2. The lowest amount of vitrification and a high amount of open porosity has been observed in the T2 tile. Tile T3 has less open porosity than tile the T2 and it has a higher level of vitrification. The highest amount of vitrification has been observed in tile T4. A high level of vitrification as well as open porosity has been observed in tile T5.

Conclusions

In this study, the effects of ulexite addition on the properties of tiles such as water absorption, strength, shrinkage, and color were investigated. With ulexite additions, tiles which have better mechanical features than the standard tiles were obtained. When mechanical features such as water absorption and bending strength were taken into consideration, the best tile was obtained with a 0.5% ulexite addition. Ulexite decreased the sintering temperature of the body causing its bending strength to increase. This is due to the fact that ulexite is a strong fluxing material and because of this it melts easily and forms a glass phase and hence flows easily to fill the porosities. As a result of this, good quality and low porosity tiles were obtained.

Tiles with standard features can be obtained at lower firing temperatures with 0.5% ulexite additions to the tile compound. A low firing temperature will lower the cost of a tile. Since ulexite is relatively cheap boron mineral it will not have a significant effect on the cost of a tile. When compared with the standard tiles, ulexite added tiles are better in terms of technical features. However, addition of ulexite in large amounts caused bubble formation in the tiles and this worsened the mechanical features of the tiles.

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References

1. R.J. Brotherton, Encyclopedia of inorganic chemistry, Wiley, New York, USA, (1995) 363-367.
2. W, Gerhartz, Ullmann's Encyclopedia of industrial chemistry, Wiley, Germany, A4, 1985 p. 263, 272, 274, 275.
3. S. Sener, G. Ozbayoglu and S. Demirci, Changes in the structure of ulexite on heating, Thermochimica Acta, 362, (2000) 107-112.
4. A. Olgun, Y. Erdogan, Y. Ayhan and B., Zeybek, Development of ceramic tiles from coal fly ash and tincal ore waste, Ceramics International, 31 (2005) 153-158.
5. S. Kurama, A. Kara, H. Kurama, Investigation of borax waste behaviour in tile production, Journal of the European Ceramic Society, 27 (2007) 1715-1720.
6. S.U. Bayca, T. Batar, E. Sayin, O Solak and B. Kahraman, The influence of coal bottom ash and tincal (boron mineral) additions on the physical and microstructures of ceramic bodies, Journal of Ceramic Processing Research, 9 (2008) 118-122.
7. A. Kartal, M. Alaca, O.F. Emrullahoglu, Investigation on the effects of a boron containing calcination product added into floor tile body receipes, Key Engineering Materials, 264-268 (2004) 1649-1652.
8. N. Ediz, H. Yurdakul ane A. Issi, Key Engineering Materials, Use of Tincal Waste as a Replacement for Calcite in Wall Tile Production, 264-268 (2004) 2457-2460.
9. O.F. Emrullahoglu, C.B. Emrullahoglu, and P. Temel, An investigation on white brick production using etibor kirka borax plant and afyon reis marble tailings, 1st International Boron Symposium, Kutahya, Turkey, (2002) 229-234.
10. B. Karasu and E. Gerede, The effect of fritted borax concentration waste on the properties of floor tile glazes, 1st International Boron Symposium, Kutahya, Turkey, (2002) 198-201.
11. A.P. Luz and S. Ribeiro, Use of glass waste as a raw material in porcelain stoneware tile mixtures, Ceramics International, 33 (2007) 761-765.
12. E.A. Uwe, A.R. Boccaccini, S.G. Cook and C.R. Cheeseman, Effect of borate addition on the sintered properties of pulverised fuel ash, Ceramics International, 33 (2007) 993-999.